

# Electrocatalytic oxidation of formaldehyde on nickel modified ionic liquid carbon paste electrode as a simple and efficient electrode

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**Abstract** Ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was used to fabricate a new ionic liquid/carbon paste electrode (IL/CPE). The general behavior of this electrode was characterized by electrochemical impedance spectroscopy, cyclic voltammetry, and scanning electron microscopy. Results showed that the IL plays an important role in improving the conductivity, reversibility, and electron transfer rate of the electrode. Nickel-modified ionic liquid/carbon paste electrode (Ni/IL/CPE) was also constructed by immersion of the IL/CPE in 1.0 M nickel sulfate solution. IL showed significant effect on the accumulation of nickel species on the surface of the electrode. The Ni/IL/CPE was applied successfully to highly efficient (current density of  $16.5 \text{ mA cm}^{-2}$ ) electrocatalytic oxidation of formaldehyde in alkaline medium. Cyclic voltammetry and chronoamperometry techniques indicated that this electrode displays a considerable electrocatalytic activity toward the oxidation of formaldehyde. The effects of different scan rates and formaldehyde concentrations on the electrocatalytic activity of this modified electrode were investigated. Finally, the rate constant for chemical reaction between formaldehyde and redox sites of the electrode was calculated.

**Keywords** Ionic liquid · Formaldehyde · Cyclic voltammetry · Carbon paste electrode · Electrocatalytic oxidation

## 1 Introduction

Ionic liquids (ILs) are stable salts, composed of an organic cation and an organic or inorganic anion, and preserved in liquid state over a wide temperature range [1, 2]. In the past few years, ILs have emerged as a frontier and novel area of research because of their excellent chemical and physical properties, such as good solvating properties, high chemical and thermal stability, non-flammability, low toxicity, almost negligible vapor pressure, high conductivity, and wide electrochemical window [3–9]. As green solvents, ILs has been proposed to be very interesting and efficient pasting binders in place of non-conductive organic binders for the preparation of carbon composite electrodes [10–12]. Using IL as a pasting binder, we can construct a new generation of carbon composite electrodes with advantages over CPE's, such as high conductivity, fast electron transfer rates, and antifouling properties [13]. There are various known hydrophobic ILs that can be used as binders for construction of these classes of electrodes. These ILs mainly consist of bis(trifluoromethylsulfonyl)imide or hexafluorophosphate anions.

The electrocatalytic oxidation of small organic molecules, such as  $\text{CH}_3\text{OH}$ ,  $\text{HCOOH}$ , and  $\text{HCHO}$ , has been widely investigated for many years and continues to be of interest due to their potential utilization as fuels in fuel cells [14–18]. The reasons for that are related to their facility of storage and handling, and mainly their high energy density. Although formaldehyde is a risk to human health, it is one of the intermediate products of methanol oxidation, and its electrochemical oxidation is important to be investigated. Moreover, it can be employed as a small model molecule in studies of the electro-oxidation of large organic molecules [19]. Formaldehyde is also used in technologically important processes such as

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electroless copper plating and the textile industries, and thus its oxidation is relevant to waste water treatment [20]. Hence, in the past few years, many reports have been published on the oxidation of HCHO under a wide range of conditions and on various electrodes [13, 20–27]. On the other hand, the use of Ni as a catalyst for electro-oxidation of this compound is of interest because it is an inexpensive metal.

Recently, we have demonstrated that incorporation of Ni(II) ions into the polymeric-modified CPE can successfully catalyze the oxidation of formaldehyde in alkaline media [28, 29]. All these results encouraged us to continue the studies with new modified electrodes to improve the efficiency of electro-oxidation of formaldehyde at the surface of these electrodes.

In this study, we combine the advantageous features of ILs, electrocatalytic properties of transition metal ions, and carbon paste technology. At first, a type of IL/CPE based on 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was constructed and investigated. Then, we incorporated Ni(II) species (as a cheap catalyst) at the surface of this new modified electrode for application to electrocatalytic oxidation of formaldehyde.

## 2 Experimental

### 2.1 Reagents and materials

The solvent used in this study was double-distilled water. Sodium hydroxide and formaldehyde were of analytical grade from Merck and used without further purification. Nickel sulfate was from Fluka and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide from Aldrich. High viscosity paraffin (density:  $0.88 \text{ g cm}^{-3}$ ) from Fluka was used as the pasting liquid for the CPE. Graphite powder (particle diameter = 0.1 mm) from Merck was used as the working electrode (WE) substrate.

### 2.2 Preparation of working electrode

A mixture of 0.15 mL paraffin and 0.10 mL IL (60:40 V/V) was added to 0.5 g of graphite powder and blended by hand mixing with a mortar and pestle for about 20 min for the preparation of carbon paste. A portion of the homogeneous paste was packed into the bottom of a glass tube (internal radius 1.7 mm) and electrical contact was provided by a copper wire connected to the paste in the inner cavity of the tube. The traditional carbon paste electrode (T-CPE) was prepared in a similar way by mixing graphite powder with only paraffin oil. The surface of electrode was smoothed on a white paper and rinsed with double-distilled water before each experiment.

### 2.3 Instrumentation

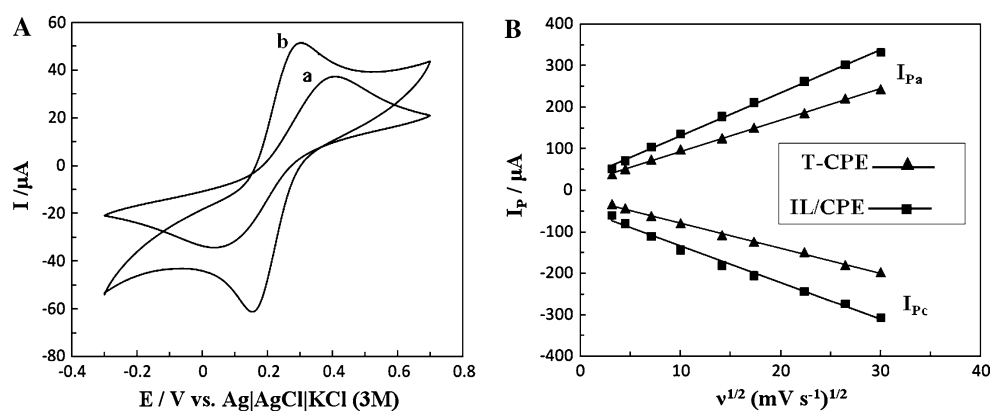
Cyclic voltammetry and chronoamperometry experiments were carried out using a potentiostat/galvanostat (Sama 500-C Electrochemical Analysis System, Sama, Iran). Electrochemical impedance spectroscopy (EIS) was performed by an AUTOLAB model PGSTST 30 using a FRA software version 4.9 (Eco chemie, the Netherlands). The electrochemical cell was assembled with a conventional three-electrode system: a well-prepared IL/CPE (3.4-mm diameter) as the WE, Ag/AgCl/KCl (3 M) as a reference electrode (Metrohm), and a platinum wire as a counter electrode.

## 3 Results and discussion

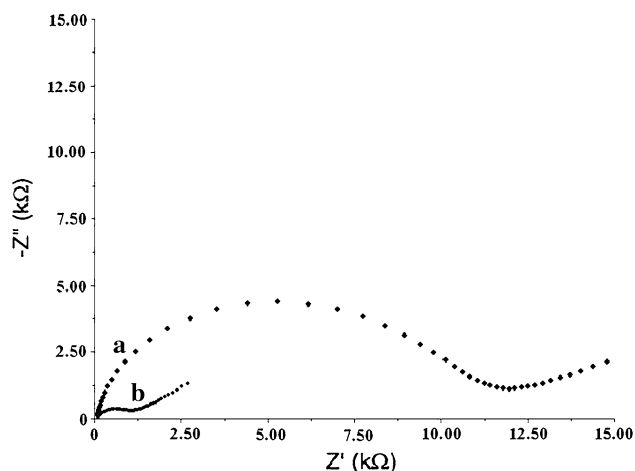
### 3.1 Electrochemical characteristics of electrodes

Potassium ferricyanide was chosen as a probe to evaluate the performance of the proposed electrodes. Fig. 1A shows the CVs of  $\text{Fe}(\text{CN})_6^{3-/4-}$  at the T-CPE (curve a) and IL/CPE (curve b). It is obvious that the substrate current response of IL/CPE was much larger than that of T-CPE.

**Fig. 1** **A** Cyclic voltammograms of T-CPE (a) and IL/CPE (b) in a solution of 5 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$  (1:1) + 0.1 M KCl at the scan rate of  $10 \text{ mV s}^{-1}$ . **B** Linear relationship of  $I_{\text{pa}}$  and  $I_{\text{pc}}$  versus  $v^{1/2}$  for T-CPE and IL/CPE

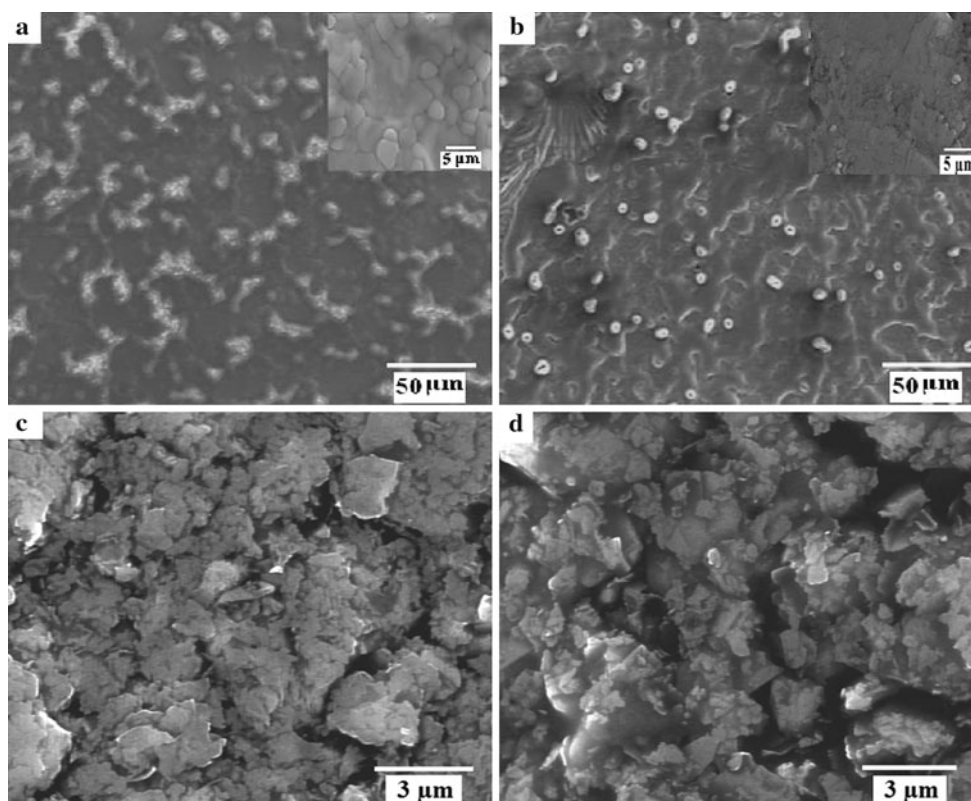


Besides, the peak potential separation, ( $\Delta E_p$ ) of 0.146 V, was observed at IL-CPE corresponding to a quasi-reversible electron transfer process. The  $\Delta E_p$  at the T-CPE was 0.369 V, indicating an irreversible electron transfer process. The effect of scan rate on the electrochemical response of these electrodes was also investigated. Linear relationship between the anodic or cathodic peak currents and  $v^{1/2}$  in Fig. 1B indicates a diffusion control process at



**Fig. 2** Nyquist plots for the Faradaic impedance measurements of a 1.0 mM solution of  $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$  (1:1) and 0.1 M KCl performed on T-CPE (a) and IL/CPE (b)

**Fig. 3** Surface morphologies of **a** T-CPE, **b** IL/CPE, **c** Ni/CPE, **d** Ni/IL/CPE



the surfaces of both the electrodes. In comparison with CV, the EIS presented more apparent differences of properties of T-CPE and IL/CPE.

Electrochemical impedance spectroscopy (EIS) is a simple and effective way to measure the charge transfer resistance ( $R_{ct}$ ) of the electrochemical reactions [30]. Fig. 2 shows the Nyquist diagrams of T-CPE (curve a) and IL/CPE (curve b) in the presence of 1.0 mM  $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$  (1:1) + 0.1 M KCl solution. It can be seen that while, T-CPE exhibits a semicircle with  $R_{ct}$  equal to 11.5 kΩ, the IL/CPE revealed a very small semicircle domain implying a very low electron transfer resistance ( $R_{ct} = 1.07$  kΩ) of the redox pair in the solution. In fact, good conductive property of the IL plays an important role in improving electron transfer rate between redox pair and electrode. It is concluded from the above mentioned results that the apparent reversibility and kinetic of the electrochemical reactions of redox pair significantly improved on IL/CPE.

Scanning electron micrographs of different electrodes including T-CPE, IL/CPE, Ni/CPE, and Ni/IL/CPE are shown in Fig. 3. The Surface topography for the T-CPE (Fig. 3a) shows that carbon powders enwrapped in paraffin oil form a granular surface. However, a more uniform surface topography was observed for IL/CPE (Fig. 3b). The uniformity of the surface shows the good adherence of the IL to graphite powder. With the addition of IL, the void spaces between the carbon and paraffin oil were filled with

conductive IL. In fact the IL is capable of better dispersing the graphite powder in the paste than the conventional paraffin oil, and therefore could better bridge the graphite flakes. SEM image of Ni/CPE (Fig. 3c) shows particles of nickel with an irregular distribution. Nickel particles on the surface of IL/CPE (Fig. 3d) have a quite different morphology that is related to the presence of IL in the electrode construction.

### 3.2 Incorporation of Ni(II) ions into the electrode

In order to incorporate Ni(II) ions at the surface of the electrode, the freshly prepared IL/CPE was placed in a well-stirred aqueous solution of 1.0 M NiSO<sub>4</sub> at an open circuit for 10 min (accumulation time,  $t_a$ , is 10 min). Then, the electrode is transferred into a cell containing 0.1 M NaOH, solution and potential cycling's were performed. This technique allows the oxide film formation in parallel to inspecting the electrochemical reactivity of the surface. Fig. 4 presents typical consecutive cyclic voltammograms in 0.1 M NaOH solution at a potential scan rate of 100 mV s<sup>-1</sup>. With an increase in the number of potential scans, three significant occurrences were observed. First, the peak currents increased gradually, indicating the progressive enrichment of the electroactive species of Ni(II) and Ni(III) in the surface, until steady state was reached. Second, the anodic and cathodic peak potentials shifted to less positive potentials and stabilized after 15 potential cyclings. This indicates the interconversion of  $\alpha$  and  $\beta$  phases of Ni(OH)<sub>2</sub> species on the surface of the electrode during consecutive cyclic voltammetry measurements. Third, oxygen evolution reaction that appears at potentials more positive than the oxidation of nickel species is markedly increased with an increase in the number of potential scans. This suggests a correlation between the

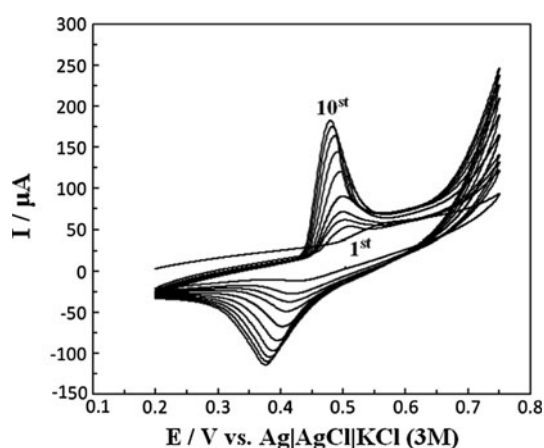
oxygen evolution and the concentration of Ni<sup>3+</sup> sites [31]. All these results are in accordance with the data reported previously in the literature [32–35].

It should be mentioned that the presence of IL in the electrode construction performed a significant effect to accumulation of nickel species on the surface of electrode. In order to support our viewpoint we carried out the experiments on the T-CPE at the identical condition of IL/CPE. After stabilization of nickel species on the surface of the electrode, results from cyclic voltammetry exhibited that the anodic and the cathodic peak currents for Ni/IL/CPE were much greater than those of Ni/CPE. Moreover, using the equation of  $\Gamma = Q/nFA$ , the surface coverage of the immobilized active substance for Ni/CPE and Ni/IL/CPE was calculated to be  $2.54 \times 10^{-9}$  and  $3.12 \times 10^{-8}$  mol cm<sup>-2</sup>, respectively.

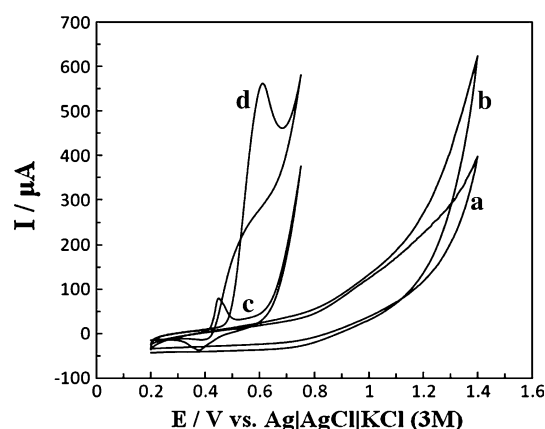
### 3.3 Electrocatalytic oxidation of formaldehyde at the Ni/IL/CPE in alkaline solution

Formaldehyde oxidation at pure IL/CPE in 0.1 M NaOH solution is very poor, and it is not possible to obtain oxidation before the discharge of the supporting electrolyte (Fig. 5b). However, nickel species at the surface of Ni/IL/CPE act as a catalyst for the oxidation of formaldehyde. It can be seen clearly in Fig. 5d that the oxidation of formaldehyde gives rise to a typical electrocatalytic response, with an increase in the anodic peak current and a decrease in the cathodic peak current. The oxidation potential of formaldehyde is more positive than the potential observed for Ni<sup>2+</sup> to Ni<sup>3+</sup> transition at the Ni/IL/CPE in the absence of formaldehyde. This suggests an interaction between the formaldehyde and the film redox centers confined at the electrode surface.

Based on these evidences, electrocatalytic oxidation of formaldehyde on Ni/IL/CPE seems to be certain via a

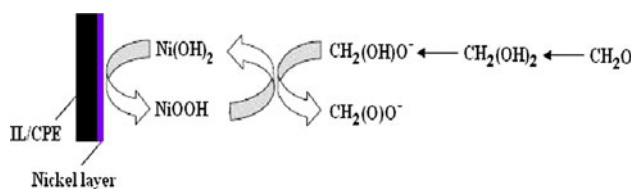
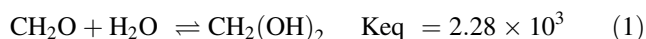


**Fig. 4** Consecutive cyclic voltammograms of Ni/IL/CPE in 0.1 M NaOH solution at the scan rate of 100 mV s<sup>-1</sup>

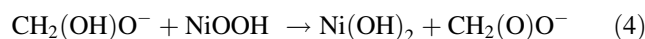
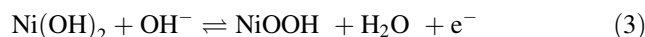
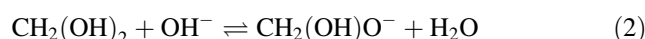


**Fig. 5** Cyclic voltammograms of IL/CPE (a, b) and Ni/IL/CPE (c, d) in the absence (a, c) and presence (b, d) of 0.023 M formaldehyde in 0.1 M NaOH solution at scan rate of 20 mV s<sup>-1</sup>

possible mechanism represented in Scheme 1. Formaldehyde in aqueous solutions exists mainly in the hydrated form, methylene glycol,  $\text{CH}_2(\text{OH})_2$ , according to the equilibrium constant for the solvation reaction [36]. Due to its  $\text{pK}_a$  of ca. 12.8 [37], the methylene glycol exists predominantly in its ionized form in 0.1 M NaOH ( $\text{pH} = 13$ ). When  $\text{CH}_2(\text{OH})\text{O}^-$  diffuses from the bulk solution to the surface of electrode, the methylene glycol ions are oxidized to  $\text{CH}_2(\text{O})\text{O}^-$  by the Ni(III) species. These stages are presented in Eqs. 1–4 with an overall reaction of (5).



**Scheme 1** Representative schematic for mechanism of formaldehyde electrooxidation at the surface of Ni/IL/CPE



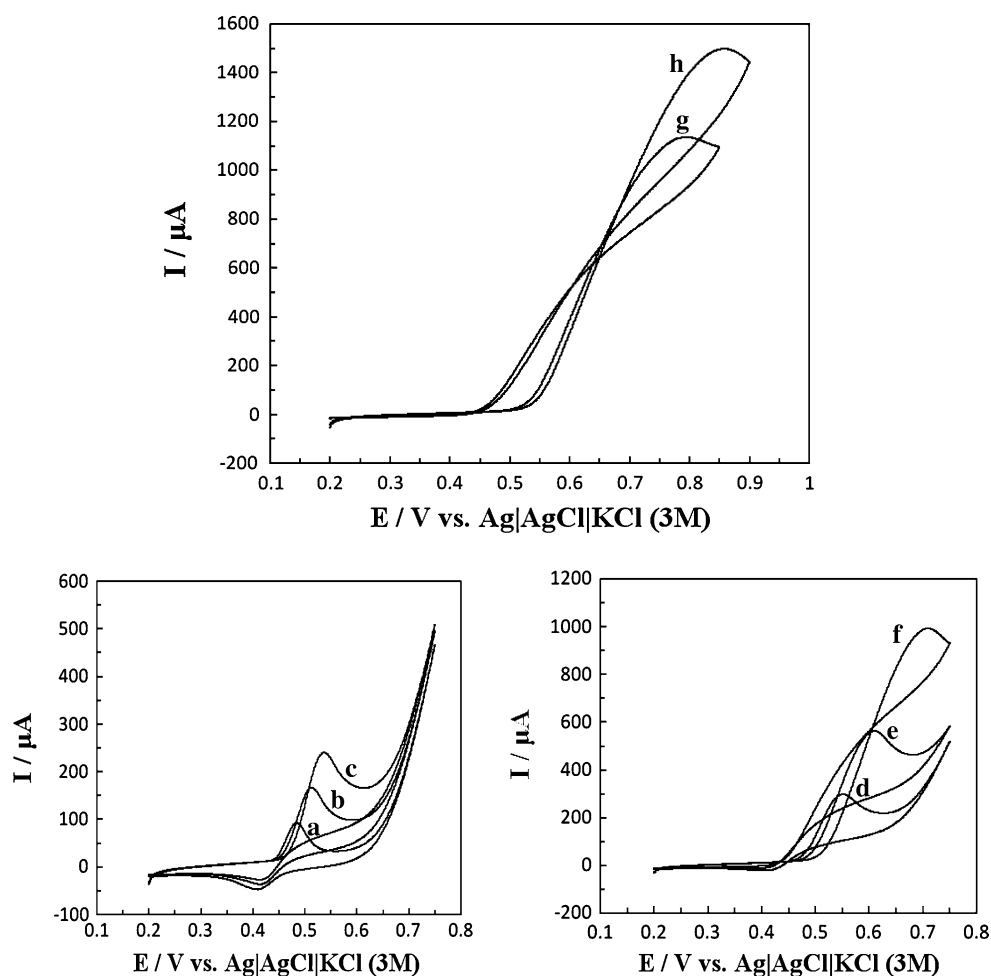
Based on Eqs. 1–4, the overall reaction can be written as



### 3.4 Effects of formaldehyde concentration and scan rate on the oxidation of formaldehyde

Effects of different concentrations of formaldehyde on the voltammetric response of Ni/IL/CPE at the scan rate of  $20 \text{ mV s}^{-1}$  are shown in Fig. 6. Increase in the concentration of formaldehyde was followed by an increase in the anodic peak current up to the concentration of 0.1 M. In the concentrations of more than 0.1 M, no remarkable increase in the anodic peak current was observed (data not shown). This can be due to the saturation of active sites of nickel catalyst on the electrode surface. In fact, oxidation process seems to be limited by the catalytic process, and its rate

**Fig. 6** Cyclic voltammograms of the Ni/IL/CPE in 0.1 M NaOH solution with different concentrations of formaldehyde: (a) 0.0, (b) 0.003, (c) 0.007, (d) 0.01, (e) 0.023, (f) 0.05, (g) 0.077, (h) 0.1 M, at scan rate of  $20 \text{ mV s}^{-1}$

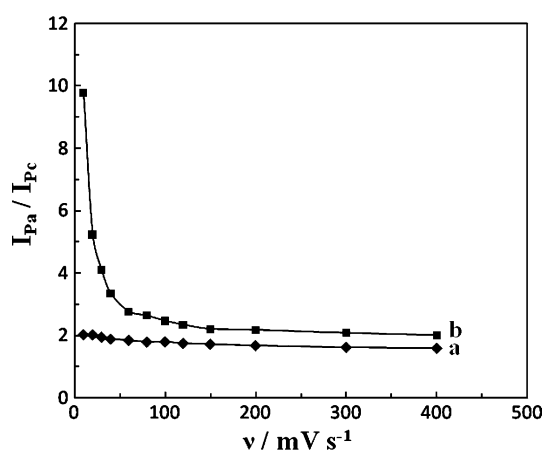




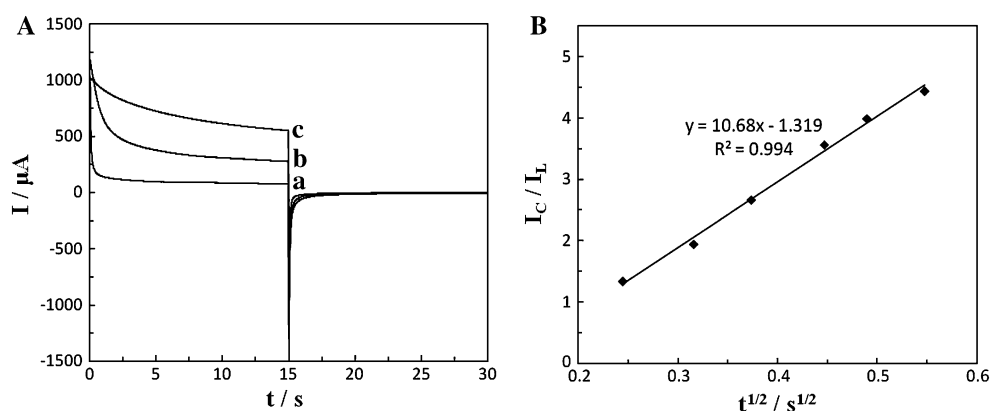
depends on the reaction between formaldehyde and Ni(III) species in the film. In order to support our conclusion, we studied the effect of scan rate on the ratio of anodic to cathodic current of Ni/IL/CPE in the absence and the presence of 0.005 M formaldehyde (Fig. 7). This figure shows that in the presence of formaldehyde, the ratio decreases significantly with the increase in the scan rate. Certainly, decrease in the time window for formaldehyde oxidation at higher scan rates avoids the facile electron transfer between formaldehyde and Ni(III) species.

### 3.5 Chronoamperometric study

Chronoamperometry technique gets more information about electro-oxidation of formaldehyde at the Ni/IL/CPE. Fig. 8A shows the current–time curves obtained by setting



**Fig. 7** Variation of the ( $I_{p_a}/I_{p_c}$ ) ratio of Ni/IL/CPE with scan rate in the absence (a) and presence of 0.005 M formaldehyde (b) in 0.1 M NaOH



**Fig. 8** **A** Chronoamperograms obtained at Ni/IL/CPE CPE in the absence of formaldehyde (a) in the presence of 0.023 M formaldehyde (b) and in the presence of 0.05 M formaldehyde (c). First and

the WE potential at 0.65 V (first step) and 0.3 V (second step), in the absence (a) and the presence (b, c) of formaldehyde. The forward and backward potential steps of the modified electrode in blank solution showed an almost symmetrical chronoamperogram for the oxidation and reduction of nickel species on the surface of the electrode. However, in the presence of formaldehyde, much greater current in the forward chronoamperometry pertains to the oxidation of formaldehyde by Ni(III) species. Chronoamperometry can also be used for the evaluation of the catalytic rate constant, according to the method described in the literature [38]:

$$I_C/I_L = \gamma^{1/2} \left[ \pi^{1/2} \operatorname{erf}(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2} \right] \quad (6)$$

where  $I_C$  and  $I_L$  are the oxidation currents of Ni/IL/CPE in the presence and in the absence of formaldehyde, respectively, and  $\gamma = kc_{ot}$  is the argument of the error function. If  $\gamma$  exceeds 1.5, then the error function is almost equal to 1, and the above equation can be reduced to

$$I_C/I_L = \gamma^{1/2} \pi^{1/2} = \pi^{1/2} (kc_{ot})^{1/2} \quad (7)$$

where  $k$ ,  $c_o$ , and  $t$  are the catalytic rate constant ( $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ ), formaldehyde concentration ( $\text{mol cm}^{-3}$ ), and time elapsed (s), respectively. From the slope of the  $I_C/I_L$  versus  $t^{1/2}$  (Fig. 8B), we can calculate the value of  $k$  for a given concentration of substrate. Thus, the mean value for  $k$  was found to be  $1.58 \times 10^6 \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$ .

Performance of the proposed electrode was investigated by a comparison between Ni/IL/CPE and some of the previously reported modified electrodes. Table 1 shows that Ni/IL/CPE displays a highly efficient electrocatalytic activity toward electrocatalytic oxidation of formaldehyde. As seen from the table, the current density of  $16.5 \text{ mA cm}^{-2}$  is greater than most of the previously reported electrodes with the exception of GC/Pt ( $18.28 \text{ mA cm}^{-2}$ ).

second potential steps were 0.65 and 0.3 V vs. Ag/AgCl, respectively. **B** Plot of  $I_C/I_L$  versus  $t^{1/2}$  derived from the data of chronoamperograms (a) and (c)

**Table 1** Comparison of the efficiency of Ni/IL/CPE with some of the previously reported electrodes for formaldehyde oxidation in alkaline medium

Electrode	$C_{\text{HCHO}}$ (mol L <sup>-1</sup> ) <sup>a</sup>	$j$ (mA cm <sup>-2</sup> ) <sup>b</sup>	$v$ (mV s <sup>-1</sup> )	Reference
Ni/P(NMA)/MCPE	0.07	4.1	20	[29]
Ni/P(1,5-DAN)/MCPE	0.17	0.76	10	[28]
Pd-CILE	0.3	9.4	100	[13]
Pt/C	0.5	10.26	50	[39]
Pt/PAANI/MWNTs/GCE	0.5	7.32	50	[19]
Pt/Pt	0.75	10.30	50	[40]
GC/Pt	0.75	18.28	50	[40]
Ni/IL/CPE	0.1	16.5	20	This study

<sup>a</sup> Maximum concentration at which the electrode responds<sup>b</sup>  $j = I_p/A$  ( $A$  = geometric surface area of substrate)

#### 4 Conclusion

In this study, we have used a hydrophobic IL for fabrication of IL/CPE and Ni/IL/CPE. The resulting IL/CPE offers some advantages over T-CPE such as high conductivity and fast electron transfer. Besides, IL is capable of better dispersing the graphite powder in the paste than the conventional paraffin oil. Nickel species were successfully stabilized on the surface of IL/CPE. IL has a prominent effect on accumulation of nickel species at the surface of electrode. The resulting Ni/IL/CPE was employed to electrocatalytic oxidation of formaldehyde in alkaline solution. Using the chronoamperometric method, catalytic rate constant between formaldehyde and Ni(III) species was calculated. This electrode exhibited highly efficient electrocatalytic activity toward formaldehyde oxidation compared to many of the previously reported electrodes.

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